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APPLICATION OF HETEROGENEOUS CATALYST OF *Meti* SHELLS (*Batissa violecea* L. von Lamark 1818) IN THE PRODUCTION OF BIODIESEL BASED ON MORINGA SEED OIL

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ABSTRACT

Meti shell contains calcium carbonate which can be calcined into CaO and used as a heterogeneous catalyst in biodiesel synthesis. This study evaluated the ability of CaO catalyst from *Meti* shell with concentrations of 1, 2, 3, 4, and 5% for the synthesis of biodiesel from Moringa seed oil at various transesterification times (1, 2, 3, and 4 hours). The presence of CaO in the *Meti* shell was indicated by diffraction at 2θ angles of 32.47°, 37.74°, 54.22°, 64.65°, and 67.67°C. Utilizing CaO 3% and a transesterification reaction time of 3 hours resulted in an Rf value corresponding to the standard biodiesel Rf ranges, i.e. 0.69 and 0.66, respectively. The synthesized biodiesel has the highest methyl oleate content of 59.16% with characteristics that have met Indonesian National Standard (SNI 04-7182-2006), including water content of 0.004%, an acid number of 0.06 mg KOH/g, saponification number 273.6 mgKOH/g, iodine number 78.678 g iodine/100 g, the cloud point is 10°C, the pour point is 21°C, however, the cetane number is still below the minimum number of 51.

Keywords: *Meti* Shells, CaO, Catalyst, Biodiesel, Rf

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INTRODUCTION

The increase in fossil fuel costs and the effects of environmental pollution lead to the emergence of alternative renewable fuels such as biodiesel.[1] The advantages of biodiesel are low emissions, harmless, non-polluting, and biodegradable.[1] Various vegetable oils can be used as essential ingredients for biodiesel, including used cooking oil, rubber seed oil, soybean oil, and Moringa seed oil.[2-8] The oil from Moringa seed can be extracted physically or chemically and can produce 38 - 40% oil.[9] Biodiesel production can be maximized by using a catalyst. Heterogeneous catalysts are more accessible to separate from the reaction mixture than homogeneous catalysts so that they can be reused, such as CaO, CaO-ZnO, K_2CO_3/ZnO, and zirconia-pillared clay.[10-14] CaO of *Meti* shells (*Batissa violecea* L. von Lamark 1818) can produce biodiesel. Ruslan et al. had been used *Meti* shells as a source of CaO for hydroxyapatite synthesis.[15] In other research, CaO 2% was used as a catalyst for biodiesel production from coconut oil at methanol to oil molar ratio of 8:1 and a temperature of 60°C for 1.5 hours with a yield of 75.02%.[16] Utilizing CaO from *Anadara granosa* shell was reported to produce biodiesel of 82.25% at a reaction time of 3 hours, a temperature of 60°C, and a catalyst concentration of 3%.[17] The utilization of a catalyst from *Meti* shells in the production of biodiesel has never been done before. This study aims to evaluate the concentration of CaO from Meti shell and transesterification reaction time on biodiesel synthesis based on Moringa seed oil.

EXPERIMENTAL

Materials

Meti shells were collected from Morowali, Central Sulawesi, Indonesia. Methanol (Merck) was used in the transesterification reaction and Thin Layer Chromatography (TLC) silica gel G60 plate (Merck) in the determination of Rf. The methyl ester profile of biodiesel was analyzed by GCMS *5977B GC/MSD Agilent* and its functional groups were determined by FT-IR Spectrometer 8201PC Shimadzu.

Heterogeneous Catalyst Preparation

The *Meti* shell was cleaned with distilled water and dried then crushed using a mortar. CaO catalysts were prepared from the calcination of *Met*i shells at 1100°C for 2 hours.[18] The degree of crystallinity of CaO was

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analyzed using XRD Rigaku Miniflex II.

Transesterification Reaction

The transesterification reaction started by activating methanol using the CaO catalyst with the concentration of 1-5% at room temperature. The edible oil was obtained from the maceration of Moringa seed powders in n-hexane solvent (1: 8 (w/v)) that was degummed at 90°C for 30 minutes. Activated methanol was mixed with Moringa seed oil with a molar ratio of 8:1 for 1-4 hours at 60±5°C. CaO was separated after the transesterification reaction had been completed. Crude biodiesel and glycerol were separated by using a separating funnel. The biodiesel impurities were removed by washing with warm distilled water (60°C). Biodiesel was passed on over anhydrous sodium sulfate. Rf value was determined using TLC with eluents composition of hexane: diethyl ether: formic acid of 8: 2: 2.[18,19] The Rf value according to the standard is then analyzed by GC-MS. The qualities of biodiesel that were analyzed include water content, acid number, cloud point, pour point, iodine value (IV), saponification number (SN), and cetane number (CN), which was calculated using eqn.-1.[20]

$$CN = 46.3 + \frac{5458}{SN} - 0.255 \times IV \qquad (1)$$

RESULTS AND DISCUSSION

CaO from *Meti* Shells

The results of XRD characterization of catalyst from *Meti* shells showed that the formation of CaO compounds was indicated by diffraction at angles of $2\theta = 32.47^o$, 37.74^o, 54.22^o, 64.65^o, and 67.67^oC (Fig.-1). The JCPDS data states that the 2θ diffraction data of calcium oxide are 32.2, 37.3, 53.8, 64.1, and 67.3^o. Calcium oxide can also be characterized by the appearance of 2θ angle between 30^o– 35^o and generally has a high intensity at 32^o and 37^o.[2,21] CaO compounds that were prepared from zinc acetate and calcium acetate reaction were characterized by the presence of high peaks at angles of 32.2°, 37.4°, 53.9°, 64.1°, and 67.4°.[12]

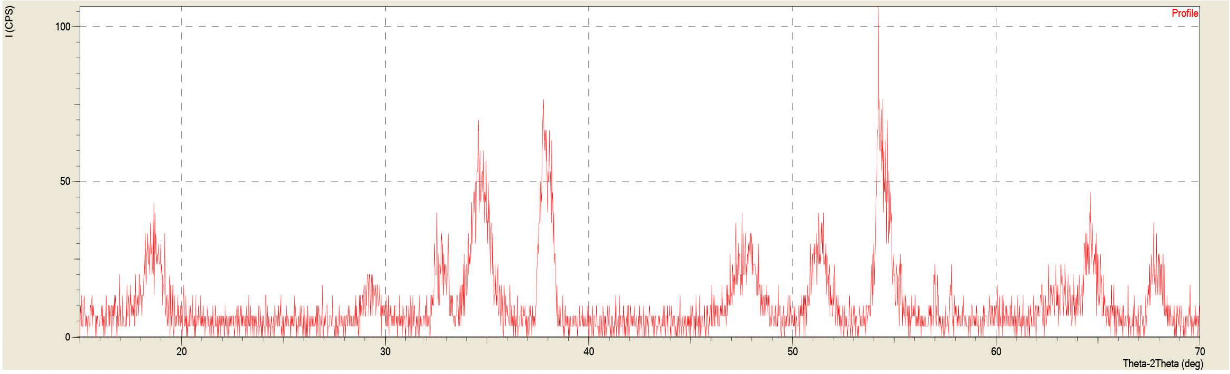

Fig.-1: Diffraction Pattern of CaO from *Meti* Shells

The high peak at an angle of $2\theta = 34.32^o$ indicates that $Ca(OH)_2$ has been formed during storage. This is presumably due to the interaction between CaO powder and water vapour in the air. Therefore, good packaging is needed during the storage and delivery of CaO for analysis. The catalytic activity of CaO is higher than $Ca(OH)_2$ and $CaCO_3$, in order that it is needed in transesterification reactions.[22] The crystallinity level of CaO obtained was also relatively high compared to the amorphous phase in the calcined *Meti* shell powder, which was 58.82% compared to 43.17% (Fig.-2).

Effect of CaO Concentration and Reaction Times

The success of the transesterification reaction can be seen from the Rf value in the TLC test. The stain with the furthest mileage or the highest Rf value on the TLC plate is a methyl ester compound.[18,19] The highest Rf value was at a catalyst concentration of 3% (0.69) (Table-1). The Rf value for biodiesel is generally in the range of 0.63 (especially for methyl oleate) until 0.8, depending on the source of the oil.[23,24] Meanwhile, in the use of other concentrations, the Rf value is still below 0.54, or it is possible that the methyl ester still contains a lot of impurities. The recent study found the best catalyst concentration in the use of 3% chicken eggshell CaO.[18] The Rf value decreased at the service of 4% and 5% catalysts, indicating that the methyl ester compound obtained had many by-products, such as residual glycerol, MAG, or DAG. This happens because using a higher concentration of heterogeneous base catalyst will cause a saponification reaction between the base and fatty acids from the oil so that soap will form, which reduces the methyl ester content obtained.[19]

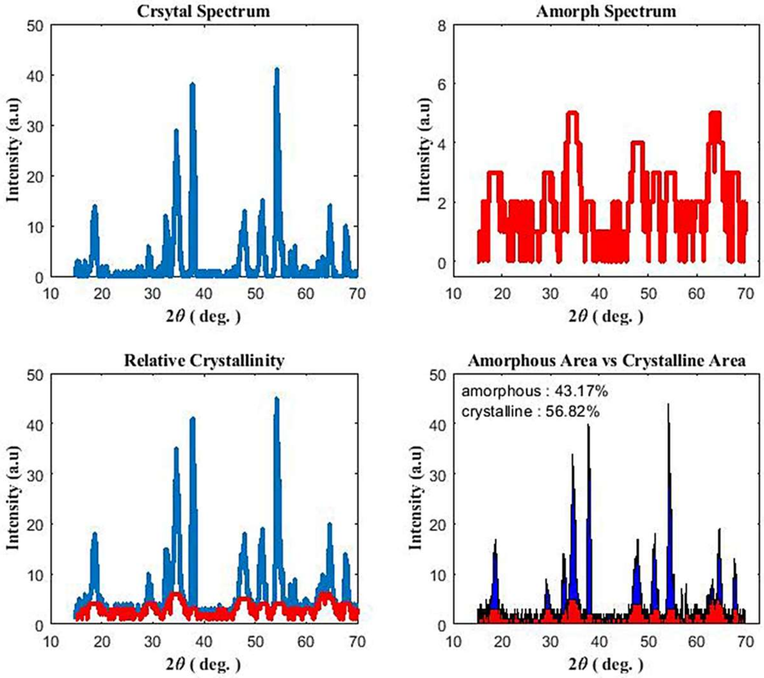

Fig.-2: The Crystallinity of Catalyst

Table-1: Rf Value of Biodiesel on Various Concentrations of Catalyst

CaO Concentration (%)	Rf
1	0.507
2	0.386
3	0.686
4	0.536
5	0.393

The reaction time of 3 hours produced the highest Rf value, which is 0.66 and is close to the Rf value of commercial biodiesel (Table-2). The reaction time of 3 hours is assumed to be the optimum condition. At 4 hours, the Rf value was also relatively high, but it was suspected that a reverse reaction had occurred so that the amount of methyl ester produced was less.

Table-2: Rf Value of Biodiesel on Various Reaction Times

Reaction times (hours)	Rf
1	0.571
2	0.543
3	0.664
4	0.643

A previous study reported that the best reaction time for making Moringa seed oil biodiesel with CaO from chicken eggshells was 2 hours.[18] The difference occurs because the source of CaO used is different, so the level of crystallinity and purity of CaO will be different. The utilization of a catalyst concentration of 3% and a transesterification time of 3 hours is the selected condition for the analysis of biodiesel composition.

GC-MS Spectrum

GC spectrum showed that the highest peak in the chromatogram was 59.16% at a retention time of 19.020 minutes (Fig.-3). The analysis results with MS predict that the area is methyl oleate (z). The same effect was also reported by Gabbia *et al.* that methyl oleate was detected at the retention time (rt) of 18.68 minutes.[25] Thus, the biodiesel obtained is dominated by methyl oleate. The main content in Moringa seed oil is oleic acid, which is up to 72.2%.[8,26]

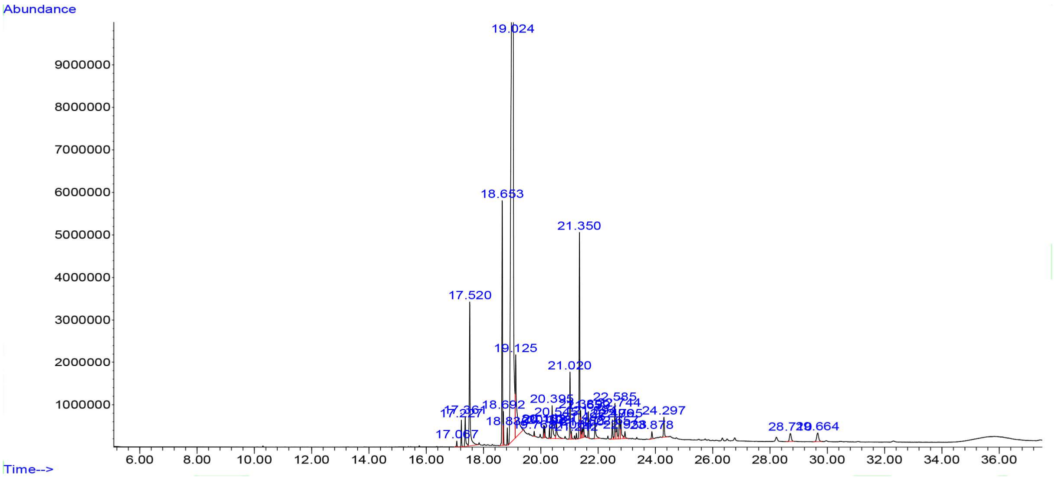

Fig.-3: Chromatogram of Methyl Ester

The MS spectrum showed that the retention time with the broadest area was interpreted as methyl oleate. Using a 3% catalyst variable and a reaction time of 4 hours obtained fragmentation patterns of m/z 55, 69, 83, 97, 111, 180, 222, and 264 (Fig.-4). The fragmentation pattern is the fragmentation pattern of methyl oleate. The same thing was obtained in another research, which succeeded in making biodiesel from *Nyamplung* seed oil with fragmentation patterns of m/z 55, 69, 83, 97, 110, 180, 222, and 264.[27] The area or percentage of methyl oleate obtained was 54.49% (3% CaO concentration) and 59.16% (3 hours reaction time). The rate of methyl oleate obtained was higher than biodiesel by using CaO from eggshells of 45.6%.[19] However, the results obtained are still lower than methyl oleate based on Moringa oil by optimization of CaO of eggshells (86.56%).[18] This indicates the need to optimize CaO catalysts from *Meti* shells to obtain methyl esters with higher concentrations. Methyl oleate, methyl palmitate, methyl palmitoleate, methyl elaidate, methyl arachidonic, and monoolein-type oil were also detected in the resulting product.

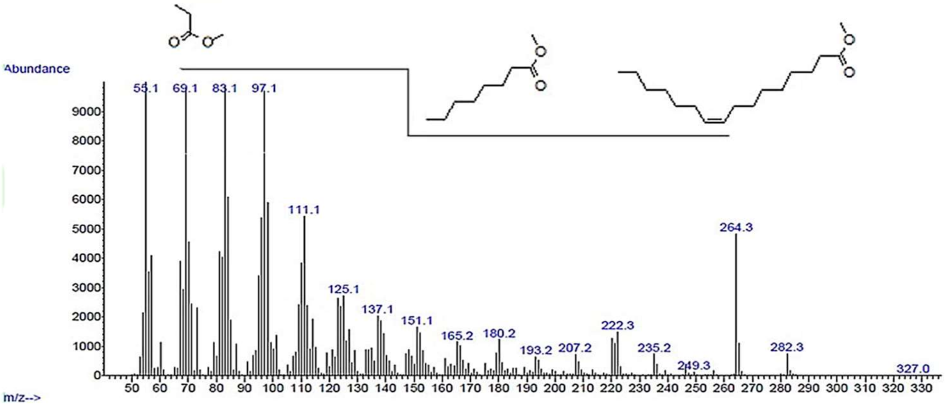

Fig.-4: MS Spectrum of Biodiesel Products

Infrared Spectrum of Biodiesel

The utilization of the FTIR spectrophotometer aims to ensure the presence of ester groups formed from fatty acid methyl esters and the absence of –OH groups as absorption from residual glycerol or MAG and DAG as by-products of transesterification. The results of functional group analysis using FTIR showed that there was absorption at a wavenumber of 1744 cm^{-1} for the treatment of catalyst concentration which was the absorption of an ester group, while at a wavenumber above 3000 $cm^{-1,}$ there was no sharp and broad peak indicating lack of –OH groups from glycerol, MAG, and DAG (Fig.-5). Ruslan *et al.* also reported that the absorption of the ester group from biodiesel was at a wavenumber of 1744 cm^{-1}.[18] The results obtained are sufficient to show that the biodiesel obtained is relatively high purity.

Biodiesel Characteristics

The biodiesel characteristics have met Indonesia biodiesel standard (SNI 04-7182-2006), such as the acid number of 0.06 mgKOH/g, the water content of 0.004%, the iodine number of 78.678 g iodine/100g, the saponification number of 273.6 mgKOH/g, the cloud point of 10°C, and the pour point of 21°C (Table-3). However, the cetane number is still below the minimum number of 51, which is only 46.19.

Table-3. Quality of Biodiesel and Indonesia Standards of Biodiesel (SNI 04-7182-2006)

Property	Result	SNI 04-7182-2006
Acid value	0.06 mgKOH/g	0.8 mgKOH/g max
Water content	0.004%	0.05% max
Iodine number	78.678 gr iod/100 gr	115 gr iod/100 gr max
Saponification number	273.6 mgKOH/g	-
Cloud point	10°C	18°C max
Pour point	21°C	28°C max
Cetane number	46.19	51 min

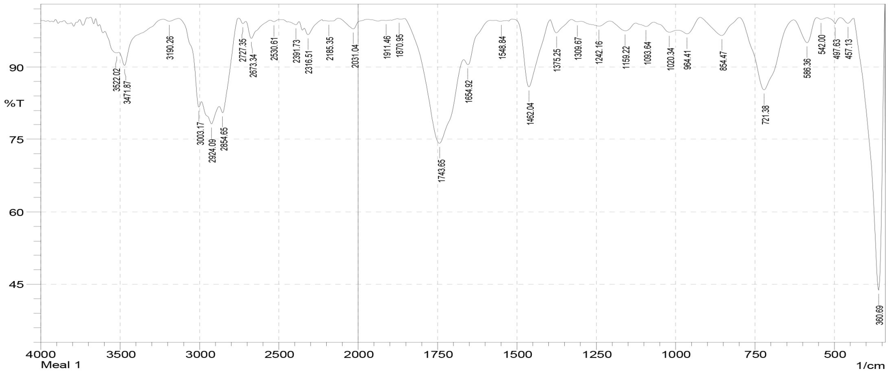

Fig.-5: FTIR Spectrum of Biodiesel Compounds

CONCLUSION

The selected condition in the production of biodiesel using CaO from *Meti* shells was a catalyst concentration of 3% and a transesterification time of 3 hours. GC-MS spectrum showed that biodiesel has the highest peak area of methyl oleate compounds at 59.16%. The biodiesel characteristics have met the standards of SNI 04-7182-2006, including acid number, water content, iodine number, saponification number, cloud point, and pour point of 0.06 mgKOH/g, 0.004%, 78.678 g iodine/100g, 273.6 mg KOH/g, 10°C, and 21°C, respectively. The cetane number is still below the minimum number of 51. Heterogeneous catalysts from *Meti* shells have good potential for use in biodiesel production.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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